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PATENT SPECIFICATION

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Int. Cl.:—C 08 d 9/10

COMPLETE SPECIFICATION

Phenolic Resins for Elastomer Compositions

We, HOOKER CHEMICAL CORPORATION of Niagara Falls, New York, United States of America, a corporation organized according to the laws of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phenolic resins and more particularly to phenolic resins in elastomeric compositions.

Phenolic resins have found use in the preparation of elastomeric compositions. However, the use of these resins has been restricted to applications such as increasing the tack of the uncured elastomeric composition, increasing the hardness of the cured or set elastomeric compositions, and as a component of an adhesive used with ordinary elastomeric compositions. Previous to the present invention the use of phenolic resins was restricted to a very small percentage of the total elastomeric composition if the composition was to remain in an elastic condition after cure. Larger amounts of such phenolic resins do further increase the tensile strength, but only at great sacrifice of the elasticity of the composition.

It has now been found that new compositions of phenolic resins permit a substantial increase in the amount of resin that may be employed in an elastomeric composition to improve tensile strength without reducing elasticity or elongation.

It is an object of this invention to provide new phenolic resins useful in elastomeric compositions. It is a further object of this invention to provide a method for making such new phenolic resins. It is still a further object of this invention to provide useful polymeric and elastomeric compositions incorporating these new phenolic resins.

In accordance with one aspect of this invention there is provided a composition of matter comprising (A) from 1 to 85 parts by weight of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde, and mixtures thereof, (2) formaldehyde and (3) phenol, in combination with (B) an elastomeric composition containing 100 parts by weight of elastomer.

In accordance with another aspect of this invention there is provided a composition of matter comprising (A) from 1 to 75 parts by weight of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde, and (3) phenol wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts by weight of an elastomer, the resin having been incorporated into the elastomeric composition while the resin was in a fusible state. In the above two compositions, the elastomer may be e.g. a copolymer of acrylonitrile and butadiene-1,3 and preferred sulphur-containing cured compositions thereof are characterised by an ultimate elongation of at least 275 percent and a tensile strength in excess of 3000 pounds per square inch.

According to another aspect, there is provided a sulphur-containing free radical cured composition of matter comprising (A) from 1 to 15 parts of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected

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from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde and (3) phenol, wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts of ethylene propylene copolymer and filled with hydrated silica, the resin having been incorporated into the elastomeric composition while the resin was in a fusible state; said composition being characterized by an ultimate elongation of at least 250 to 350 percent and a tensile strength of 1500 to 2500 pounds per square inch.

According to a still further aspect, there is provided a sulphur containing cured composition of matter comprising from 1 to 20 parts of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde and (3) phenol, wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts of styrene butadiene copolymer and filled with carbon black; the resin having been incorporated into the elastomeric composition while the resin was in a fusible state; said composition being characterized by an ultimate elongation of at least 275 to 375 percent and a tensile strength of 2500 to 3500 pounds per square inch.

According to a still further aspect, there is provided a method comprising (A) mixing at a temperature between about 125 and 275 degrees Fahrenheit (1) 1 to 85 parts of a fusible phenol-aldehyde resin containing the residues of (a) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, propionaldehyde, isobutyraldehyde, isopentaldehyde and mixture thereof (b) formaldehyde and (c) phenol together with a cross-linking amount of hexamethylene tetramine and (2) an elastomeric composition containing 100 parts of elastomer and (B) curing the resulting mixture at a temperature between about 250 and 345 degrees Fahrenheit.

The elastomers embraced within the scope of this invention are those polymeric materials used in the rubber manufacturing industry and commonly referred to by the class name as "rubber", including both natural and synthetic elastomers. The synthetic elastomers some of which have already been mentioned include styrene-butadiene rubber, acrylonitrile-butadiene rubber, polyisoprene, polychloroprene rubber and ethylene-propylene rubber. Unless otherwise indicated, the term "natural rubber", as used in this application, is understood to mean those elastomers derived from the Hevea Brasiliensis. The concept of the interchangeability of styrene-butadiene copolymer, natural rubber and polymerized isoprene recognized in the rubber article manufacturing industry, is also recognized in this application.

Generally, to be useful, an elastomer should be modified by the inclusion of other chemicals. In a simple composition, curing agents such as sulfur and zinc oxide are added to the elastomer to produce an unfilled composition which when cured by the application of heat, is useful in a limited number of applications. Additionally, the cure or cross-linking agent may be a free radical curative such as an organic peroxide. Most elastomeric compositions, however, to be useful must be further modified by the inclusion of modifiers such as pigments for color, chemicals to protect the elastomer from degradation, other curatives to alter the curing characteristics of the composition, fillers to impart greater strength or merely to lower the cost of the composition and softeners or plasticizers. Among the fillers which have been used to increase the tensile strength and hardness of the elastomeric composition are carbon black, phenol-formaldehyde resins, clay and metallic oxides.

The typical phenolic resin used in compounding elastomers is based upon the reaction of formaldehyde with an excess of phenol to produce a novolac which thereafter may be oil modified. When added to an elastomeric composition along with sufficient methylene bridge donors and with the application of heat, the phenol resins resinify into hard, permanently set materials which contribute greatly to the stiffness of the elastomeric composition.

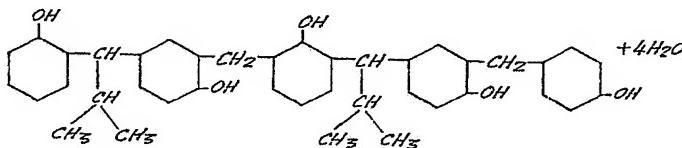
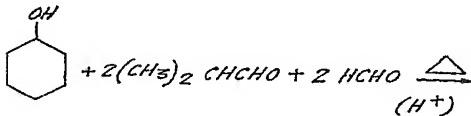
It has now been found that by utilizing higher carbon chain length aldehydes instead of formaldehyde in a phenolic resin reaction, a considerably more flexible, yet equally reinforcing material can be obtained for use in elastomeric compositions. The aldehydes which confer these desirable qualities and which are "higher carbon chain length aldehydes" are those of the group consisting of isobutyraldehyde, isopentaldehyde, acetaldehyde and propionaldehyde. For convenience, this group will be intended too, when isobutyraldehyde is mentioned, unless otherwise noted. Hitherto the use of isobutyraldehyde in phenolic resins has not been considered. The mole concentration of isobutyraldehyde to be employed is determinable from two considerations, namely,

the rate at which the resin cures and the amount of isobutyraldehyde required to achieve the desired changes in the physical properties in the rubber composition.

High concentrations of isobutyraldehyde in the phenolic resin mixture will resinify. However, the reaction is sluggish and the resulting resins are slow curing. Low concentrations of isobutyraldehyde are sufficient to produce noticeable changes in the physical properties of the elastomeric compound. Especially successful practical resins may be prepared when the mole per cent of isobutyraldehyde is from 20 to 80 per cent (preferably 25 to 80 per cent) of the total aldehyde content employed in condensing the phenols, the balance being formaldehyde. A mixture of the higher chain length aldehydes may be employed to achieve still greater flexibility with less variation of the resins physical properties.

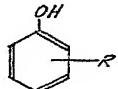
The quantity of the invented resins to be admixed with an elastomeric composition will vary over wide ranges depending upon the exact elastomeric composition properties desired. It has been found that up to 85 PHR (Parts by weight per hundred parts of elastomer in the elastomeric composition), preferably 1 to 75 P.H.R. of our resin containing 80 mole per cent isobutyraldehyde may be successfully employed in elastomeric compositions. Similar advantages may be obtained by varying the mole ratio of isobutyraldehyde with a corresponding adjustment in the total amount of resin employed.

The amount of aldehyde to be condensed with the phenol may be varied to prepare condensates of varying molecular weights and the viscosity of the finished resin may be controlled by regulation of the molecular weight thereof. These products are known as novolacs and are deficient in methylene linkages to the extent that they are properly termed linear polymers. As such, novolacs will soften and fuse into a mass with application of heat. Additional methylene linkages are required to cross-link these polymers and make them infusible. Preferably, the amount of total aldehyde (i.e. higher carbon chain length aldehyde and formaldehyde) varies from 0.5 to 1.0 mol per mol of the phenol when a mono or difunctional phenol is used. In instances where a trifunctional phenol is used, the preferred upper limit of total aldehyde may be about 0.85 mol per mol of phenol so as to prevent formation of insoluble and infusible condensates. When a resin formulation is prepared so that the total aldehyde ratio to phenol is comparable to a formalin (37.2% formaldehyde content by weight) to phenol ratio of 66.4% by weight, a resin with an average chain length of 5 phenol units results. A typical reaction is illustrated below:



The remaining mole per cent of aldehyde to make resins of this invention can be formaldehyde which may be in aqueous solution (formalin) or in any of its low polymeric forms such as paraformaldehyde or trioxane.

Examples of phenols which may be used in preparing phenol/aldehyde/isobutyraldehyde condensates for use in practicing the invention include phenol itself or substituted phenols having the following general formula:



where R may be F, Cl, Br or a suitable substituent selected from the following:

- (a) Alkyl groups of 1 to 18 carbon atoms in any of their isomeric forms and substituted on the phenolic nucleus in the ortho-, meta or para positions;
- (b) Alicyclic groups of 5 to 18 carbon atoms such as cyclohexyl, cyclopentyl, methyl cyclohexyl, butyl-cyclohexyl;

(c) Aromatic or aralkyl groups of 6 to 18 carbon atoms such as phenyl, alpha-methyl benzyl, benzyl, cumyl;

(d) Alkyl, alicyclic, aryl and aralkyl ketones wherein the hydrocarbon is defined as hereinbefore.

5 (e) Alkyl, alicyclic, aryl and aralkyl carboxylic groups wherein the hydrocarbon is as defined hereinbefore.

Suitable substituted phenols include the following: para-tertiary-butylphenol, para-secondary-butylphenol, para-tertiary hexylphenol, para-isooctyl-phenol; para-phenylphenol, para-benzylphenol, para-cyclohexylphenol, para-decyl-phenol, para-dodecyl-phenol, para-tetra-phenol, para-octa-decyl-phenol, para-nonyl-phenol, para-methyl-phenol, para-beta-naphthyl-phenol, para-alpha-naphthyl-phenol, para-penta-decyl-phenol, para-cetyl-phenol, para-cumyl phenol, para-hydroxy acetophenone, para-hydroxy benzophenone, a phenol alkylated with limonene, a phenol alkylated with oleic acid, as well as the corresponding ortho and meta derivatives such as meta-butyl phenol and ortho-butyl phenol, as well as mixtures thereof.

10 From the foregoing, it is apparent that substantially any phenol may be used in practicing the present invention provided it has a reactive phenolic hydroxyl group capable of directing methylene linkages to produce a condensate. The pure refined phenols may be used, but this is not always necessary. For instance, phenols may be alkylated and then reacted with an aldehyde to produce a crude product which may contain some polyalkylated as well as non-alkylated phenols. Mixtures of phenols mentioned herein also may be used.

15 The use of isobutyraldehyde in the novolac preparation indicates the employment of strong, concentrated acids as catalyst such as sulfuric or hydrochloric acid. Wetting agents of the anionic type such as sodium alkyl aryl sulfonate are very useful as secondary catalysts.

20 Among the most practical methods of preparation of the invented compositions is that which involves the addition of the isobutyraldehyde prior to addition of formaldehyde since a concentrated and strong acid is utilized with isobutyraldehyde to promote complete reaction with the phenol. The addition and reaction of formaldehyde prior to the isobutyraldehyde would be less satisfactory and would dilute the catalyst concentration and limit the reflux temperature of the reaction mixture (to about 100 degrees centigrade). Under these conditions, isobutyraldehyde would not usually be fully reacted. Alternatively, it is possible to add and react the formaldehyde, remove the water by distillation, and then add the isobutyraldehyde and react it with the phenolic compound. However, this procedure is much more cumbersome and time consuming.

25 A mixture of phenol, catalyst and wetting agent, such as an alkyl aryl sodium sulfonate or other suitable anionic compound of equivalent action is charged to reaction vessel and is heated to 100 degrees centigrade. The isobutyraldehyde is added slowly, allowing the temperature of the mix to rise so that general reflux is obtained. After the isobutyraldehyde is added the mixture is refluxed until the reaction is completed. Thereafter formaldehyde is slowly added to the reaction mixture at 100 degrees centigrade maintaining general reflux conditions throughout the addition 30 and then the reaction mixture is refluxed until completed. Afterward the catalyst may be neutralized and the novolac distilled to the desired endpoint. The reaction may be modified to proceed under temperatures upwards of 150 degrees centigrade at pressures upwards of 100 psi for a suitable time, e.g., one and one-half hours, until the desired degree of condensation has taken place. Thereafter excess reactant, water, 35 and so forth are removed and the molten resin is discharged from the vessel.

40 The resin is then ground to desired particle size and the desired amount of methylene link donor material such as hexamethylene-tetramine is admixed with it. A preferred amount of hexamethylenetetramine comprises 7 to 17 percent of the weight of the resin. The basic resin is now ready for use in elastomeric compositions.

45 The elastomeric composition is prepared by using conventional compounding and mixing equipment of the rubber manufacturing industry. A description of a preparation procedure follows.

50 The elastomer is physically plasticized, "masticated", or "broken down" by a process which comprises subjecting the elastomer to a severe mechanical shearing stress. Under such conditions the elastomer gradually becomes softer and more readily deformable. Mechanically the change may be produced by a "rubber" mill or an internal mixer, for example, a Banbury mixer.

55 Acetonitrile-butadiene is effectively masticated on a rubber mill by milling the elastomer for 5 to 10 minutes on a cool, tight mill. Temperatures up to about 125

degrees Fahrenheit are considered to be satisfactory for masticating. Tight is employed in the usual rubber manufacturing sense, that is, the space between mill rolls required to subject the elastomer to severe mechanical shearing stress is small when compared to normal distance employed while mixing the composition. A suitable clearance might be one eighth of an inch.

When the elastomeric composition is mixed on a mill, the masticated rubber is then banded on the slow roll and the zinc oxide and sulfur are added followed according to the preferred procedure, by the addition of the basic resin above described. Alternatively the resin could be added after the addition of softener which is described below. Good dispersion is important. Cutting and blending with cuts three-fourths across the roll gives uniform mixing; however, the batch should not be cut when dry pigments are present in the rolling bank. Half of the filling pigment is then added, cut and blended into the batch. The second half may then be added and dispersed. Softeners, waxes, accelerators and organic acid activators, such as stearic acid, are added in that order. The batch is then cut, blended and refined until it is of uniform composition. Time to complete the mixing is based on the time to properly blend in all ingredients and yet not initiate the cross-linking of the composition. Typical mixing temperatures for mill mixing of elastomeric compositions is from 125 to 180 degrees Fahrenheit while temperatures employed by internal mixers may even exceed 275 degrees Fahrenheit.

The compositions of Examples 15 to 57 were prepared using the above described method.

After making the mixtures of described components by a process such as that described, the elastomeric composition is made into useful articles by forming and cross-linking by the application of controlled amounts of heat and pressure, temperatures of 250 to 345 degrees Fahrenheit and pressures of 25 to 100 pounds per square inch for 2 to 60 minutes being useful.

Although many formulations of elastomeric compositions within the invention may be made, some typical compositions are shown in Tables 2 to 6. An extensive collection of elastomeric compositions, ingredients and references are contained in The Vanderbilt Rubber Handbook (6th Edition), R T Vanderbilt Company, New York, N.Y., 1958.

The invention is illustrated by the following examples which are intended to exemplify but not to limit the scope of this invention.

Tables I and IA which contain Examples 1 to 14, show some formulations and properties of the resins of this invention.

Examples 15 to 21 in Table 2 illustrate the effect of resins prepared with isobutyraldehyde in an unfilled acrylonitrile/butadiene copolymer. All elastomeric formulations are expressed in terms of 100 parts of rubber hydrocarbon (PHR). Physical test data was obtained in accordance with ASTM procedures. Outstanding improvement of tensile strength with slight changes in other physical properties is shown by resins of Example 3 (60 mole per cent isobutyraldehyde), Example 4 (50 mole per cent isobutyraldehyde), and Example 5 (40 mole per cent isobutyraldehyde) in Examples 17, 18, and 19 respectively.

Table 3 compares a widely used resin of the rubber article manufacturing industry against that of the present invention. The resin of Example 4 (50 mole per cent isobutyraldehyde) was tested at various concentrations (20 to 100 PHR) in the same unfilled acrylonitrile/butadiene formulation of Table 2. Resins of Examples 9, 12 and 14 were tested at the 50 PHR level. An exceptional increase of tensile strength is shown by formulations containing up to 80 parts resins of our invention while the elongation values remain comparable.

Table 4 demonstrates the utility of our invention in hard kaolin clay filled acrylonitrile-butadiene copolymer compositions while Table 5 illustrates use in carbon black filled styrene butadiene copolymer composition.

We have found our invention suitable for use with ethylene propylene copolymers as shown in Table 6.

TABLE No. 1
RESIN FORMULATIONS & PHYSICAL PROPERTIES

EXAMPLE	1	2	3	4	5	6	7
NOVOLAC FORMULATION (Parts by weight)							
Phenol	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sulfuric Acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
*Nacconol (Registered Trade Mark) NRSF	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Isobutyraldehyde (IBA)	57.6	51.7	34.4	28.7	23.0	5.7	—
Formalin (37%)	—	6.5	26.0	32.25	39.0	58.6	66.4
MOLE % IBA/CH₃O	100/0	90/10	60/40	50/50	40/60	10/90	0.100
PHYSICAL PROPERTIES							
Melting Point, Shrink, °C.	65	73	65	76	73	67	73
Melting Point, Clear, °C.	72	84	79	82	81	77	81
I.P. Flow 0.2 gm. mm.	250	132	140	121	128	152	110
0.3 gm. mm.	—	180	186	174	174	231	154
FINAL RESIN (Parts by weight)							
Novolac	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hexamethylene tetramine	12.0	12.0	12.0	12.0	12.0	12.0	12.0
PHYSICAL PROPERTIES							
Cure @ 150°C, sec.	260—265	200—205	130—135	115—120	110—115	73—78	63—68
Cure @ 165°C, sec.	113—115	84—86	61—63	53—54	55—57	34—36	31—33
Melting Point, Shrink, °C.	64	71	69	78	73	67	69
Melting Point, Clear, °C.	76	85	83	88	88	87	89
I.P. Flow, 0.5 gm. mm.	135	103	92	86	82	76	52
pH (20% resin water soln.)	8.9	8.9	8.7	8.3	8.6	8.6	8.5

*alkyl aryl sodium sulfonate wetting agent, National Aniline Div. Allied Chemical Corp.

TABLE No. 1A
RESIN FORMULATIONS & PHYSICAL PROPERTIES

EXAMPLE	8	9	10	11	12	13	14
NOVOLAC FORMULATION (Parts by weight)							
Phenol	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sulfuric Acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Nacconol (Trade Mark)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Isopentylaldehyde	—	—	—	—	—	—	177.5
Formalin (37%)	498.0	332.0	166	498.0	332.0	166.0	498.0
Acetaldehyde	91.0*	182.0	273	—	—	—	—
Propionaldehyde	—	—	—	119.5	239.0	358.5	—
Mole % Higher Aldehyde/ CH_2O	25/75	50/50	75/25	25/75	50/50	75/25	25/75
PHYSICAL PROPERTIES							
Melting Point, Shrink, °C.	72	73	68	64	60	52	61
Melting Point, Clear, °C.	81	84	77	73	68	63	70
I.P. Flow 0.2 gm. mm.	112	114	141	105	148	242	161
0.3 gm. mm.	156	152	184	134	208	>250	214
FINAL RESIN (Parts by weight)							
Novolac	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hexamethylene tetramine	12.0	12.0	12.0	12.0	12.0	12.0	12.0
PHYSICAL PROPERTIES							
Cure @ 150 °C., sec.	68-70	79-81	93-95	76/78	110-112	76-78	76-78
Cure @ 165 °C., sec.	33-35	39-41	43-45	38/40	44-46	36-38	36-38
Melting Point, Shrink, °C.	69	72	71	60	58	61	61
Melting Point, Clear, °C.	98	84	89	77	70	76	76
I.P. Flow, 0.5 gm. mm.	52	70	81	78	110	80	80
pH (20% resin water soln.)	8.6	8.5	8.5	8.8	8.7	8.8	8.8

* Considered as 3 moles of Acetaldehyde.

TABLE No. 2
COMPARISON OF ISOBUTYRALDEHYDE/FORMALDEHYDE MOLE RATIOS
IN UNFILLED ACRYLONITRILE/BUTADIENE COPOLYMER COMPOSITION

EXAMPLE	15	16	17	18	19	20	21
Mole % IBA/CH ₃ O	100/0	90/10	60/40	50/50	40/60	10/90	0/100
Hycar (Trade Mark) 1001*	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Resin Example #1	—	—	—	—	—	—	—
Resin Example #2	—	50.0	—	—	—	—	—
Resin Example #3	—	—	50.0	—	—	—	—
Resin Example #4	—	—	—	50.0	—	—	—
Resin Example #5	—	—	—	—	50.0	—	—
Resin Example #6	—	—	—	—	—	50.0	—
Resin Example #7	—	—	—	—	—	—	50.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
PHYSICAL PROPERTIES, Press cure 20' @ 300°F.							
Tensile Strength, psi	2340	2510	3448	3963	3212	2573	1987
Elongation, %	323	341	413	404	362	363	250
Modulus (100% Elongation) psi	301	317	356	391	482	474	687
Tear Resistance, lbs/in.	296	312	449	375	413	546	510
Shore Hardness	A70	A71	A77	A79	A82	A87	A88

*High Acrylonitrile Content
Acrylonitrile/butadiene Copolymer
Mfr. B.F. Goodrich Co.

TABLE No. 3

EXAMPLE	22	23	24	25	26	27	28	29
Hycar (Trade Mark) 1001	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Durez (Trade Mark) 12687*	20.0	—	40.0	—	50.0	—	60.0	—
Resin Example #4	—	20.0	—	40.0	—	50.0	—	60.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<hr/> PRESS CURED 20' @ 300°F.								
Tensile Strength, psi	1360	1889	1950	3520	2004	3960	2360	3900
Elongation, %	424	507	328	439	280	402	259	360
Modulus @ 100% E, psi	381	224	692	349	1052	395	1497	551
Tear Resis., lbs./in.	149	335	214	375	323	382	507	338
Shore Hardness	A68	A66	A84	A79	A93	A77	**D42	A81
<hr/> Hycar (Trade Mark) 1001								
Stearic Acid	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc Oxide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Durez (Trade Mark) 12687	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Resin Example #4	80.0	—	100.0	—	—	—	—	—
Resin Example #9	—	80.0	—	100.0	—	—	—	—
Resin Example #12	—	—	—	—	—	50	—	—
Resin Example #14	—	—	—	—	—	—	50	—
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<hr/> PRESS CURED 20' @ 300°F.								
Tensile Strength, psi	2820	2522	3503	1870	929	3612	4093	3963
Elongation, %	191	240	124	132	745	380	383	404
Modulus @ 100% E, psi	2502	652	3200	1254	120	468	574	391
Tear Resis., lbs./in.	631	366	—	292	121	410	429	375
Shore Hardness	D57	A83	D64	A88	A56	A79	A82	A79

* Two stage phenol formaldehyde resin with hexamethylene tetraamine, Hooker Chemical Corp.

** Shore "A" Hardness greater than 95, therefore, Shore "D" Hardness must be obtained.

TABLE No. 4
A COMPARISON IN CLAY LOADED NITRILE RUBBER STOCK

EXAMPLE	39	39	40	41	42
Hycar (Trade Mark) 1001	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Dixie (Trade Mark) Clay*	100.0	100.0	100.0	100.0	100.0
Durez (Trade Mark) 12987	—	20.0	—	30.0	—
Resin Example #4	—	—	20.0	—	30.0
Sulfur	1.5	1.5	1.5	1.5	1.5
<hr/>					
PRESS CURED 20' (@ 300°F.					
Tensile Strength, psi	2400	2863	3208	3257	2804
Elongation, %	201	192	199	151	175
Modulus (@ 100% E, psi.	810	1544	1710	2368	1468
Tear Resistance, lbs./in	359	404	430	429	374
Shore Hardness	A81	A85	A89	A91	A92

* Hard Kaolin Clay, R.T. Vanderbilt Co.

TABLE No. 5
A COMPARISON OF PHENOLIC RESINS IN CARBON BLACK
LOADED STYRENE-BUTADIENE RUBBER STOCK

EXAMPLE	43	44	45	46	47	48	49
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0	100.0
HAF Black	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Durez (Trade Mark) 13355**	—	5.0	—	10.0	—	20.0	—
Resin Example #4	—	—	5.0	—	10.0	—	20.0
Altax*(Trade Mark)	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PRESS CURED 30' @ 300 °F.							
Tensile Strength, psi	3265	3300	3345	3035	3157	2505	2510
Elongation, %	430	371	352	336	307	277	289
Modulus @ 100% E, psi	331	441	510	552	749	683	898
Tear Resistance	345	313	380	306	368	287	340
Shore Hardness	A68	A72	A75	A76	A80	A83	A85

* Benzothiazyl Disulfide, R. T. Vanderbilt Co.

** Two stage phenol-formaldehyde resin Hooker Chemical Corp.

TABLE No. 6
A COMPARISON OF PHENOLIC RESINS AS REINFORCING AGENTS
IN HI-SIL FILLED ETHYLENE-PROPYLENE RUBBER

EXAMPLE	50	51	52	53	54
EPR 404*	100.0	100.0	100.0	100.0	100.0
Hi-Sil (Trade Mark) 233*	60.0	60.0	60.0	60.0	60.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Durez (Trade Mark) 12687	—	5.0	10.0	20.0	—
Durez (Trade Mark) 13355	—	—	—	—	20.0
Resin Example #4	—	—	—	—	—
Di-Cup (Trade Mark)	2.7	2.7	2.7	2.7	2.7
Sulfur	0.32	0.32	0.32	0.32	0.32
<hr/>					
PRESS CURED 40' @ 300°F.					
Tensile Strength, psi	1532	2205	2203	1878	1830
Elongation, %	712	646	703	605	696
Modulus @ 100% E, psi	217	361	344	332	289
Tear Resis., lbs./in.	424	364	344	332	289
Shore Hardness	A80	A89	A88	A91	A80
<hr/>					
EPR 404 (Enjay)	100.0	100.0	100.0	100.0	100.0
Hi-Sil (Trade Mark) 233	60.0	60.0	60.0	60.0	60.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Durez (Trade Mark) 12687	—	—	—	—	—
Durez (Trade Mark) 13355	—	—	—	—	—
Resin Example #4	—	—	—	—	—
Di-Cup (Trade Mark)	5.0	10.0	20.0	20.0	20.0
Sulfur	2.7	2.7	2.7	2.7	2.7
0.32	0.32	0.32	0.32	0.32	0.32
<hr/>					
PRESS CURS 40' @ 300°F.					
Tensile Strength, psi	2012	2218	1837	1837	1837
Elongation, %	625	702	667	667	667
Modulus @ 100% E, psi	391	347	377	377	377
Tear Resis., lbs./in.	326	354	314	314	314
Shore Hardness	A91	A90	A90	A90	A90

* Ethylene-Propylene copolymer, Enjay Chem. Div. of Humber Oil Corp.
** Precipitated Hydrated Silica, Pittsburgh Plate Glass Co.

That the exceptional compatibility of the present resins with elastomeric compositions permits the incorporation of substantially large amounts of resin therein, while causing no significant change of stress-strain properties, is of great importance to the rubber products manufacturing industry. Thus, a means has been provided for reducing the amount of elastomer required in a composition, yet with the achievement of comparable results. Moreover, in many cases, for example with an acrylonitrile-butadiene copolymer unfilled compositions, the physical properties are significantly improved.

5 10 WHAT WE CLAIM IS:—

10 15 1. A composition of matter comprising (A) from 1 to 85 parts by weight of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopent-aldehyde, propionaldehyde, and mixtures thereof, (2) formaldehyde and (3) phenol, in combination with (B) an elastomeric composition containing 100 parts by weight of elastomer.

15 20 2. A composition of matter comprising (A) from 1 to 75 parts by weight of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopent-aldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde and (3) phenol wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts by weight of elastomer, the resin having been incorporated into the elastomeric composition while the resin was in a fusible state.

25 25 3. A composition according to Claim 1 or 2 wherein the elastomer is a copolymer of acrylonitrile and butadiene-1,3.

4. A composition according to Claim 1 or 2 wherein the elastomer is a copolymer of ethylene and propylene.

5. A composition according to Claim 1 or 2 wherein the elastomer is a copolymer of styrene and butadiene-1,3.

30 30 6. The composition according to Claim 1 or 2 wherein the resin additionally contains between 7 and 17 percent by weight of hexamethylenetetramine.

7. A sulphur-containing cured composition according to Claim 3, said composition being characterized by an ultimate elongation of at least 275 percent and a tensile strength in excess of 3000 pounds per square inch.

35 35 8. A sulphur containing free radical cured composition of matter comprising (A) from 1 to 15 parts of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde and (3) phenol, wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts of ethylene propylene copolymer and filled with hydrated silica, the resin having been incorporated into the elastomeric composition while the resin was in a fusible state; said composition being characterized by an ultimate elongation of at least 250 to 350 percent and a tensile strength of 1500 to 2500 pounds per square inch.

40 40 9. A sulphur containing cured composition of matter comprising from 1 to 20 parts of a phenol-aldehyde resin containing the residues of (1) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, isobutyraldehyde, isopentaldehyde, propionaldehyde and mixtures thereof, (2) formaldehyde and (3) phenol, wherein from 25 to 80 mole percent of the aldehyde radicals are derived from the higher carbon chain length aldehyde in combination with (B) an elastomeric composition containing 100 parts of styrene butadiene copolymer and filled with carbon black; the resin having been incorporated into the elastomeric composition while the resin was in a fusible state; said composition being characterized by an ultimate elongation of at least 275 to 375 percent and a tensile strength of 2500 to 3500 pounds per square inch.

45 50 55 55 10. A method comprising (A) mixing at a temperature between about 125 and 275 degrees Fahrenheit (1) 1 to 85 parts of a fusible phenol-aldehyde resin containing the residues of (a) a higher carbon chain length aldehyde selected from the group consisting of acetaldehyde, propionaldehyde, isobutyraldehyde, isopentaldehyde and mixtures thereof (b) formaldehyde and (c) phenol together with a cross-linking amount of hexamethylene tetramine and (2) an elastomeric composition containing 100 parts of elastomer and (B) curing the resulting mixture at a temperature between about 250 and 346 degrees Fahrenheit.

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11. The method according to Claim 10 wherein the elastomer is a copolymer of acrylonitrile and butadiene-1,3.

12. The method according to Claim 10 wherein the elastomer is a copolymer of styrene and butadiene-1,3.

5 13. A composition of matter according to Claim 1 substantially as herein described with reference to the Examples. 5

14. A cured composition according to Claim 7, 8 or 9 substantially as herein described with reference to the Examples.

15. A method according to Claim 10 substantially as herein described with reference to the Examples. 10

16. A product made by a method according to Claim 10, 11, 12 or 15.

MEWBURN ELLIS & CO.,

Chartered Patent Agents,

70/72, Chancery Lane, London, W.C.2.

Agents for the Applicants.

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